

## PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF SUPERFINE SILVER PARTICLE

## (57)Abstract:

PROBLEM TO BE SOLVED: To easily and stably obtain superfine silver particles having a specific grain size or below by dissolving silver chloride into ammonia water in such a manner that a specific silver concn. may be attained and adding a reducing agent to this soln. in the presence of a protective colloid of a specific concn. range, then stirring the soln. to execute liquid phase reduction.

SOLUTION: The silver chloride of a raw material is dissolved as amine chloride silver in the ammonia water. The silver concn. in the resulted soln. is specified to a range of 1 to 100g/l. The protective colloid is added to this soln. before the addition of the reducing agent thereto to prevent the flocculation of the reduction deposited superfine silver particles. Gelatin, etc., are usable as the protective colloid and the concn. thereof is specified to 0.5 to 50g/l. Hydrazine, etc., are usable as the reducing agent. The amt. of the agent to be added is preferably about 1 to 5 equiv. of the silver in the soln. The amine chloride is reduced to silver when the soln. is stirred after the reducing agent is added thereto. The superfine silver particles having the grain size below 0.1  $\mu\text{m}$  is thus obtd.

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the silver ultrafine particle characterized by adding and agitating a reducing agent under existence of protective colloid in this solution, and obtaining a silver ultrafine particle with a particle size of 0.1 micrometers or less by liquid phase reduction after dissolving a silver chloride so that it may become aqueous ammonia with 1 - 100 g/l by silver concentration.

[Claim 2] The manufacture approach of the silver ultrafine particle according to claim 1 characterized by the concentration of the protective colloid in said solution being 0.5 - 50 g/l.

[Claim 3] The manufacture approach of the silver ultrafine particle according to claim 1 or 2 characterized by adding 1-5Eq of reducing agents to the silver in said solution.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach particle size manufactures stably the ultrafine particle of silver 0.1 micrometers or less.

[0002]

[Description of the Prior Art] From the former, the end of silver dust is mainly used as an electrical conducting material of the conductive paste used for formation of a thick film circuit etc. For example, after printing a circuit pattern, an electrode, etc. on a ceramic substrate using conductive paste including the end of silver dust, calcinating and forming a thick film circuit is performed.

[0003] In this conductive paste, it excels in conductivity, so that the end of silver dust which is the electric conduction component is a particle, and moreover, formation of a thin fine circuit is attained. Therefore, recently, offer of a silver ultrafine particle 0.1 micrometers or less is demanded for particle size as the end of silver dust for conductive paste.

[0004] The approach of pyrolyzing silver acetate is proposed by JP,5-156326,A as an approach of manufacturing the silver dust end of an ultrafine particle. However, the approach by the pyrolysis of this silver acetate was not easy to manufacture when the large-scale manufacturing installation in which a controlled atmosphere is possible was needed, in order to perform a pyrolysis to the bottom of reduced pressure or a non-oxidizing atmosphere, and it had a problem also from the point of safety.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims to let particle size offer the approach of manufacturing it being simple and stably a silver ultrafine particle 0.1 micrometers or less, without using a large-scale manufacturing installation in view of such a conventional situation.

[0006]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, after dissolving a silver chloride so that it may become aqueous ammonia with 1 - 100 g/l by silver concentration, the manufacture approach of the silver ultrafine particle which this invention offers adds and agitates a reducing agent under existence of protective colloid in this solution, and is characterized by obtaining a silver ultrafine particle with a particle size of 0.1 micrometers or less by liquid phase reduction.

[0007]

[Embodiment of the Invention] In the manufacture approach of the silver ultrafine particle of this invention, a silver chloride AgCl is used as a raw material, this silver chloride is dissolved in aqueous ammonia, and it is referred to as chlorination amine [silver (NH<sub>3</sub>) Ag 2] Cl. Next, a reducing agent is added agitating the solution of this chlorination amine silver, and a silver ultrafine particle is obtained by \*\* which returns chlorination amine silver by the liquid phase. In this invention, since it is based on such wet reduction processing, detailed silver nucleation is possible and, finally a silver ultrafine particle with a particle size of 0.1 micrometers or less can be obtained.

[0008] that from which the silver chloride used as a raw material is obtained by the usual process — it is — good — for example, the reaction of a silver nitrate and a hydrochloric acid — or it is easy to be obtained by the reaction of a silver nitrate and a chloride solution. Moreover, although either a dry matter or a non-dry matter is OK as a silver chloride, when the solubility to aqueous ammonia is taken into consideration, a non-dry matter is desirable.

[0009] The silver chloride of a raw material is dissolved in aqueous ammonia as chlorination amine silver. Since the silver ultrafine particle generated when the productivity of a silver ultrafine particle is very low in less than 0.1 g/l, and the silver concentration in the solution obtained is unreal and exceeded 100 g/l conversely condenses, a silver ultrafine particle with a particle size of 0.1 micrometers or less is not obtained. Therefore, silver concentration contained as chlorination amine silver in a solution should be made the range of 1 – 100 g/l, and let it preferably be the range of 5 – 50 g/l.

[0010] The ammonia concentration of the aqueous ammonia used for the dissolution of a silver chloride does not need to adhere to especially concentration, if the crystal of a silver chloride does not deposit in the solution when a silver chloride is dissolved that the ammonia more than the reaction equivalent required to dissolve all the silver chlorides of a raw material as chlorination amine silver should just contain so that silver concentration may serve as the range of the above 1 – 100 g/l. However, when the solubility of a silver chloride, the final total amount of solutions, etc. are taken into consideration, aqueous ammonia of about 25% of concentration usually marketed is desirable.

[0011] In this chlorination amine silver solution, protective colloid is added, before adding a reducing agent. The reason for adding protective colloid is for making it the silver ultrafine particle which carried out the reduction deposit not condense. Since a change remarkable in distribution of the silver ultrafine particle which deposits even if it will be easy to condense a silver ultrafine particle and will exceed 50 g/l conversely, if it becomes less than 0.5 g/l is not seen, as for the concentration of protective colloid, it is desirable to consider as the range of 0.5 – 50 g/l. Moreover, as a class of protective colloid, it is usually used for the purpose of condensation prevention, and can be easy to use gelatin, gum arabic, poly vinyl alcohol, etc.

[0012] Thus, a reducing agent is added and agitated in the adjusted solution, and chlorination amine silver is returned to silver. If the reducing agent to be used has sufficient reducing power to silver, it cannot ask the class, for example, a hydrazine, a sodium borohydride, formalin, etc. can be used for it. Even if the addition of a reducing agent uses a superfluous amount for remainder, it is [ that what is necessary is just the amount to which the silver in a solution is returned completely ] meaningless. Therefore, the addition of a reducing agent has desirable about 1–5Eq to the silver in a solution, and its 1.5–3.5Eq is still more desirable.

[0013] Like usual, it is made to distribute in alcohol or an organic solvent, and the silver ultrafine particle obtained in this way is saved and conveyed, in order to carry out separation recovery from a solution with the usual means, such as centrifugal separation, and to prevent condensation.

[0014]

[Example]

18g of silver chlorides of 10g of example 1 silver purity was dissolved agitating at a room temperature to 1l. of aqueous ammonia of 25% of concentration, and the solution of chlorination amine silver was obtained. 100ml of poly vinyl alcohol water solutions of concentration 25 g/l was added to the obtained chlorination amine silver solution as protective colloid.

[0015] Next, it added having dissolved the 1.5g sodium borohydride in 30ml of sodium-hydroxide solutions of concentration 200 g/l as a reducing agent, and agitating the solution of the obtained reducing agent in the above-mentioned chlorination amine silver solution, and churning aging was performed for 30 minutes.

[0016] Consequently, when the silver granule child generated and gazed at the obtained silver granule child with the scanning electron microscope in the above-mentioned solution, it was a silver ultrafine particle with a mean particle diameter of 0.06 micrometers.

[0017] 90g of silver chlorides of 50g of example 2 silver purity was dissolved agitating at a room temperature to 1l. of aqueous ammonia of 25% of concentration, and the solution of chlorination

amine silver was obtained. 100ml of poly vinyl alcohol water solutions of concentration 25 g/l was added to the obtained chlorination amine silver solution as protective colloid.

[0018] Next, it added having dissolved the 7.5g sodium borohydride in 150ml of sodium-hydroxide solutions of concentration 200 g/l as a reducing agent, and agitating the solution of the obtained reducing agent in the above-mentioned chlorination amine silver solution, and churning aging was performed for 30 minutes.

[0019] Consequently, when the silver granule child generated and gazed at the obtained silver granule child with the scanning electron microscope in the above-mentioned solution, it was a silver ultrafine particle with a mean particle diameter of 0.08 micrometers.

[0020]

[Comparative Example(s)] 198g of silver chlorides of 110g of silver purity was dissolved agitating at 40 degrees C to 1l. of aqueous ammonia of 25% of concentration, and the solution of chlorination amine silver was obtained. 300ml of gelatin water solutions of concentration 150 g/l was added to the obtained chlorination amine silver solution as protective colloid.

[0021] Next, it added having dissolved 16.5g of sodium borohydrides in 330ml of sodium-hydroxide solutions of concentration 200 g/l as a reducing agent, and agitating the solution of the obtained reducing agent in the above-mentioned chlorination amine silver solution, and churning aging was performed for 30 minutes.

) [0022] When gazed at the silver granule child obtained in the above-mentioned solution with the scanning electron microscope, he was a silver granule child with a mean particle diameter of 0.3 micrometers. Since the silver concentration in a chlorination amine silver solution was more superfluous than 110 g/l, this is based on what the silver granule child who deposited condensed.

[0023]

[Effect of the Invention] Since it is based on the wet process using liquid phase reduction according to this invention, it can carry out using an easy reactor, and reaction actuation is also easy and particle size can manufacture stably a silver ultrafine particle 0.1 micrometers or less.

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(54) 【発明の名称】 銀超微粒子の製造方法

(57) 【要約】

【課題】 大掛かりな製造装置を用いることなく、粒径が $0.1\mu\text{m}$ 以下の銀超微粒子を、簡便に且つ安定的に製造する方法を提供する。

【解決手段】 塩化銀をアンモニア水に銀濃度で $1\sim 100\text{g/l}$ となるように溶解した後、この溶液に保護コロイドの存在下で還元剤を加えて攪拌し、溶液中の塩化アミン銀を液相還元して粒径 $0.1\mu\text{m}$ 以下の銀超微粒子を得る。

## 【特許請求の範囲】

【請求項1】 塩化銀をアンモニア水に銀濃度で1～100g/lとなるように溶解した後、この溶液に保護コロイドの存在下で還元剤を加えて攪拌し、液相還元により粒径0.1μm以下の銀超微粒子を得ることを特徴とする銀超微粒子の製造方法。

【請求項2】 前記溶液中の保護コロイドの濃度が0.5～50g/lであることを特徴とする、請求項1に記載の銀超微粒子の製造方法。

【請求項3】 還元剤を前記溶液中の銀に対して1～5当量加えることを特徴とする、請求項1又は2に記載の銀超微粒子の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、粒径が0.1μm以下の銀の超微粒子を安定的に製造する方法に関するものである。

## 【0002】

【従来の技術】 従来から、厚膜回路等の形成に用いる導体ペーストの導電材料として、主に銀粉末が使用されている。例えば、銀粉末を含む導体ペーストを用いて、セラミックス基板上に回路パターンや電極等を印刷した後、焼成して厚膜回路を形成することが行われている。

【0003】 かかる導体ペーストにおいては、その導電成分である銀粉末が微粒子であるほど導電性に優れ、しかも薄く細かい回路の形成が可能となる。そのため最近では、導電ペースト用の銀粉末として、粒径が0.1μm以下の銀超微粒子の提供が要望されている。

【0004】 超微粒子の銀粉末を製造する方法としては、酢酸銀を熱分解する方法が特開平5-156326号公報に提案されている。しかし、この酢酸銀の熱分解による方法は、減圧下若しくは非酸化性雰囲気下において熱分解を行うため、雰囲気調整が可能な大掛かりな製造装置を必要とする上、製造が容易ではなく、安全性の点からも問題があった。

## 【0005】

【発明が解決しようとする課題】 本発明は、このような従来の事情に鑑み、大掛かりな製造装置を用いることなく、粒径が0.1μm以下の銀超微粒子を、簡便に且つ安定的に製造する方法を提供することを目的とする。

## 【0006】

【課題を解決するための手段】 上記目的を達成するため、本発明が提供する銀超微粒子の製造方法は、塩化銀をアンモニア水に銀濃度で1～100g/lとなるように溶解した後、この溶液に保護コロイドの存在下で還元剤を加えて攪拌し、液相還元により粒径0.1μm以下の銀超微粒子を得ることを特徴とする。

## 【0007】

【発明の実施の形態】 本発明の銀超微粒子の製造方法においては、原料として塩化銀AgClを使用し、この塩

化銀をアンモニア水に溶解して塩化アミン銀 $[Ag(NH_3)_2]Cl$ とする。次に、この塩化アミン銀の溶液を攪拌しながら還元剤を加え、塩化アミン銀を液相で還元することによって、銀の超微粒子を得るものである。本発明では、このような湿式の還元処理によるので、銀の微細な核形成が可能であり、最終的に粒径0.1μm以下の銀超微粒子を得ることができる。

【0008】 原料として使用する塩化銀は通常の製法により得られるもので良く、例えば硝酸銀と塩酸の反応によって、又は硝酸銀と塩化物溶液の反応によって得られるもので良い。また、塩化銀は乾燥物又は未乾燥物のどちらでも良いが、アンモニア水への溶解性を考慮すると未乾燥物が好ましい。

【0009】 原料の塩化銀は、アンモニア水に塩化アミン銀として溶解させる。得られる溶液中の銀濃度が0.1g/l未満では銀超微粒子の生産性が極めて低く非現実的であり、逆に100g/lを越えると生成した銀超微粒子が凝集するため、粒径0.1μm以下の銀超微粒子が得られない。従って、溶液中に塩化アミン銀として含まれる銀濃度は1～100g/lの範囲とすべきであり、好ましくは5～50g/lの範囲とする。

【0010】 塩化銀の溶解に使用するアンモニア水のアンモニア濃度は、原料の塩化銀が全て塩化アミン銀として溶解されるのに必要な反応当量以上のアンモニアが含有されていれば良く、塩化銀を銀濃度が上記1～100g/lの範囲となるように溶解したとき、その溶液中に塩化銀の結晶が析出しなければ、特に濃度にこだわる必要はない。しかし、塩化銀の溶解性や、最終的な全溶液量等を考慮すると、通常市販されている濃度25%程度のアンモニア水が好ましい。

【0011】 この塩化アミン銀溶液には、還元剤を加える前に保護コロイドを添加する。保護コロイドを添加する理由は、還元析出した銀超微粒子が凝集しないようにするためである。保護コロイドの濃度は、0.5g/l未満になると銀超微粒子が凝集しやすく、逆に50g/lを越えても析出する銀超微粒子の分散に顕著な変化が見られないため、0.5～50g/lの範囲とすることが好ましい。また、保護コロイドの種類としては、凝集防止の目的で通常使用されているもので良く、例えば、ゼラチン、アラビアゴム、ポリビニールアルコール等を使用することができる。

【0012】 このようにして調整した溶液に、還元剤を加えて攪拌し、塩化アミン銀を銀に還元する。使用する還元剤は、銀に対して十分な還元力を有するものであればその種類を問わず、例えば、ヒドラジン、水素化ホウ素ナトリウム、ホルマリン等を用いることができる。還元剤の添加量は、溶液中の銀が完全に還元される量であれば良く、余りに過剰な量を使用しても無意味である。従って、還元剤の添加量は、溶液中の銀に対して1～5当量程度が好ましく、1.5～3.5当量が更に好まし



い。

【0013】かくして得られた銀超微粒子は、遠心分離等の通常的手段により溶液から分離回収し、凝集を防ぐために通常のごとくアルコールや有機溶媒中に分散させて保存、輸送する。

【0014】

【実施例】

実施例1

銀純分10gの塩化銀18gを、濃度25%のアンモニア水1lに室温で攪拌しながら溶解し、塩化アミン銀の溶液を得た。得られた塩化アミン銀溶液に、保護コロイドとして濃度25g/lのポリビニールアルコール水溶液を100ml加えた。

【0015】次に、還元剤として1.5gの水素化ホウ素ナトリウムを濃度200g/lの水酸化ナトリウム溶液30mlに溶解し、得られた還元剤の溶液を上記塩化アミン銀溶液に攪拌しながら添加し、30分間攪拌熟成を行った。

【0016】その結果、上記溶液中には銀粒子が生成し、得られた銀粒子を走査型電子顕微鏡で観察したところ、平均粒径0.06 $\mu$ mの銀超微粒子であった。

【0017】実施例2

銀純分50gの塩化銀90gを、濃度25%のアンモニア水1lに室温で攪拌しながら溶解し、塩化アミン銀の溶液を得た。得られた塩化アミン銀溶液に、保護コロイドとして濃度25g/lのポリビニールアルコール水溶液を100ml加えた。

【0018】次に、還元剤として7.5gの水素化ホウ

素ナトリウムを濃度200g/lの水酸化ナトリウム溶液150mlに溶解し、得られた還元剤の溶液を上記塩化アミン銀溶液に攪拌しながら添加し、30分間攪拌熟成を行った。

【0019】その結果、上記溶液中には銀粒子が生成し、得られた銀粒子を走査型電子顕微鏡で観察したところ、平均粒径0.08 $\mu$ mの銀超微粒子であった。

【0020】

【比較例】銀純分110gの塩化銀198gを、濃度25%のアンモニア水1lに40℃で攪拌しながら溶解して、塩化アミン銀の溶液を得た。得られた塩化アミン銀溶液に、保護コロイドとして濃度150g/lのゼラチン水溶液を300ml加えた。

【0021】次に、還元剤として水素化ホウ素ナトリウム16.5gを濃度200g/lの水酸化ナトリウム溶液330mlに溶解し、得られた還元剤の溶液を上記塩化アミン銀溶液に攪拌しながら添加し、30分間攪拌熟成を行った。

【0022】上記溶液中に得られた銀粒子を走査型電子顕微鏡で観察したところ、平均粒径0.3 $\mu$ mの銀粒子であった。これは、塩化アミン銀溶液中の銀濃度が110g/lよりも過剰であったため、析出した銀粒子が凝集したことによる。

【0023】

【発明の効果】本発明によれば、液相還元を利用した湿式処理によるため、簡単な反応装置を用いて実施でき且つ反応操作も容易であって、粒径が0.1 $\mu$ m以下の銀超微粒子を安定的に製造することができる。

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